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Another discussion of such fibres is found under the heading "Segmented Polyurethanes" at page 613 of *Handbook of Textile Fibres* by J. Gordon Cook, 5th Ed. Merrow Publishing Company 1984. Further

description of elastanes and their applications can be
found in "Synthesefasern: Grundlagen, Technologie,
Verarbeitung und Anwendung", B von Falkei (editor),
Verlag Chemie (1981). Commercially available elastanes
5 are well known, in particular as sold under the name
LYCRA®, a registered trade mark of DuPont de Nemours
and Company. Patents relating to such fibres include
US-A-5000899, US-A-5288779 and US-A-5362432.

The deposition of perfume onto garments and
10 other fabrics during laundering has been established
for many years. Perfume is incorporated into laundry
products such as detergent compositions for fabric
washing and rinse conditioners for softening the
fabrics.

15 Although the perfume serves to cover the
base odour of such a product and to give the unused
product an attractive fragrance, it also deposits on
the fabric.

Certain perfumes have the ability to provide
20 deodorant action against body odour, either when
directly applied to human skin, or when included in a
laundry product. Such perfumes are described in EP-B-
3172, US-A-4304679, US-A-4278658, US-A-4134838, US-A-
4288341 and US-A-4289641, US-A-5482635 and US-A-
25 5554588.

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We have now found that a number of fragrance materials used in perfumery are able to deposit and then be retained better on spandex fibres than on a number of other textile fibres.

Delivery of fragrance materials to fabric can take place during washing, as is well known. The present invention appreciates that the application of perfume to textiles containing spandex fibres can be utilised in the treatment of textiles which are newly made - that is to say textile goods which have never been worn as garments by a consumer.

Therefore in one aspect the present invention provides a method of treating textile which is yarn or fabric containing spandex fibres, comprising contacting the textile with a perfume so that the perfume is deposited on the fabric. Preferably, the fabric is unworn. It may have been made up into a garment.

In a related second aspect, the invention provides textile which is yarn or fabric containing spandex fibres, having perfume deposited on the textile. Preferably, the fabric is unworn. It may have been made up into a garment.

We have observed that a range of fragrance materials deposited on such textiles will still be

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Preferably, the fabric is unworn.

deodorant property.

The various aspects of this invention, preferred forms and materials useful therein will now be discussed in greater detail.

The textiles to which this invention relates include spandex fibres. As mentioned earlier, this term denotes a manufactured fibre in which the fibre forming substance is a long chain synthetic polymer compound composed of at least 85% of a segmented polyurethane.

Thus the polymer which is spun into spandex fibres is a copolymer incorporating urethane linkages. Generally the polymer contains so-called soft (i.e. lower melting) segments which may be polyalkylene ethers or polyesters and so-called hard (i.e. higher melting) segments which are portions derived from the reaction of an isocyanate and a chain extender which is typically a diamine.

The soft segments may be poly(tetramethylene)ethers, possibly containing substituted tetramethylene glycol residues as described in US-A-5000899. Organic diisocyanates which may be used include conventional diisocyanates, such as diphenylmethane-4,4'-diisocyanate, also known as methylene-bis(4-phenylisocyanate) or "MDI", 2,4-tolylene diisocyanate, methylene-bis(4-cyclohexylisocyanate), isophorone diisocyanate, tetramethylene-p-xylylene diisocyanate, and the like. MDI is preferred.

Chain extenders used in producing the hard segment of the fibres preferably include one or more of ethylenediamine (EDA), 1,3-propylenediamine, 1,4-cyclohexanediamine, hydrogenated m-phenylenediamine (HPMD), 2-methylpentamethylene diamine (MPMD) and 1,2-propylene diamine. More preferably, the chain extender is one or more of ethylenediamine, 1,3-

Spandex fibres with poly(tetramethylene)

Spandex fibres are generally mixed with

other fibres such as cotton, polyamide, wool, polyester and acrylics and made into yarn which is then made into fabric. The content of spandex fibres is usually in a range from 0.5% by weight of the yarn or fabric up to 50%, more usually from 1 to 30% by weight of the yarn or fabric.

A wide range of garments may contain spandex fibres in the fabric, including active sports wear, intimate apparel, hosiery and a variety of ready to wear casual clothing.

The textiles which are treated with a perfume composition prior to wearing may be yarn which is later made into fabric, or may be fabric in the form of a web or lengths from a web which have not yet been made into garments, or may possibly be garments.

Preferably the treatment with a perfume composition is carried out while treating with other material in a conventional process step, especially a

However, the perfume composition may be included directly into the spandex fibre. A fabric may be made using the spandex fibre alone.

The materials which may be applied to fabric in a conventional finishing treatment include resins to confer stiffness, fabric stability or permanent press, fabric softeners, flame retardants, fabric brighteners, anti-snap agents, materials to confer soil or stain resistance and water repellants.

Treatment with a perfume composition in accordance with this invention can be carried out by including the perfume composition in the liquor used in a process as above.

The amount of perfume deposited on the fabric in a treatment step carried out on fabric will generally be from 0.001% to 1% by weight of the fabric.

Fragrance materials

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We have found that a range of fragrance

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Category B

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A requirement for $\log_{10}P$ of 2.5 or more calls for materials which are somewhat hydrophobic.

Materials of low Kovats index tend to be volatile and are not retained well on many fibres.

We have found that when perfumery materials have partition coefficient as above and a relatively high value of Kovats index, deposition and retention

on spandex tends to be greater than on other fibres.
Preferably therefore, the perfume composition contains
at least 50 wt %, better at least 70 or 80 wt % of
materials from the categories above.

5 We have found that there is a particularly
high enhancement of deposition and retention on
spandex, compared to other fibres, with materials
within the above categories and having a Kovats index
of not more than 1600. These sub-sets of categories A
10 and B may be termed categories A' and B'. Preferably
therefore, the perfume composition contains at least
10 wt%, better at least 20 wt% or 25 wt% of such
materials. In some preferred perfumes the amount of
fragrance materials from categories A' and B' is at
15 least 40 wt% in total.

Such fragrance materials are of mid-range
volatility (i.e. intermediate between the volatile
perfume materials used as "top-notes" and the
materials of low volatility which are customarily used
20 as "base notes" in perfumes). These materials of mid-
range volatility are often not perceptible on other
fabrics such as cotton, polyamide and polyester after
washing and drying.

Category A includes alcohols of general
25 formula ROH where the hydroxyl group may be primary,
secondary or tertiary, and the R group is an alkyl or

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Common Fragrance and Flavor Materials by Bauer, Garbe and Surburg, VCH Publ., 2nd edition (1990), and *Perfume and Flavour Materials*, Steffen Arctander, published in two volumes by the author (1969).

5	Examples of fragrance materials in category A'
	1-(2'-tert-butylcyclohexyloxy)-butan-2-ol*
	3-methyl-5-(2',2',3'-trimethylcyclopent-3-enyl)-pentan-2-ol*
	4-methyl-3-decen-5-ol*
10	amyl salicylate*
	2-ethyl-4(2',2',3-trimethylcyclopent-3'-enyl)but-2-enol* (Bangalol, TM)
	borneol*
	carvacrol*
15	citronellol*
	9-decenol*
	dihydroeugenol*
	dihydrolinalol*
	dihydromyrcenol
20	dihydroterpineol *
	eugenol
	geraniol*
	hydroxycitronellal*
	isoamyl salicylate*
25	isobutyl salicylate*
	isoeugenol*
	linalol
	menthol*
	nerolidol*

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	nerol*
	para tert-butyl cyclohexanol*
	phenoxanol*
	terpineol
5	tetrahydrogeraniol*
	tetrahydrolinalol
	tetrahydromyrcenol
	thymol*
	2-methoxy-4-methylphenol (Ultravanil, TM)
10	(4-isopropylcyclohexyl)-methanol*

Some examples of fragrance materials which are in category A but which have Kovats index above 1600 (so as to fall outside category A') are:

- benzyl salicylate
- 15 cyclohexyl salicylate
- hexyl salicylate
- patchouli alcohol
- farnesol

Category B is esters, ketones, aldehydes, nitriles or ethers which have an octanol-water partition coefficient whose common logarithm ($\log_{10}P$) is at least 2.5, and a Kovats index of at least 1300 (non-polar phase).

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Ingredients of Category B are of general formula RX, where X may be in a primary, secondary or tertiary position, and is one of the following groups:

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-COA, -OA, -CO₂A, -CN or -CHO. The groups R and A are hydrocarbon residues, cyclic or non-cyclic and optionally substituted. In some forms of this invention, category B excludes any material with a free hydroxy group, so that where a hydroxyl group is present, the material should be considered only for Category A membership. Typically, the materials of Category B with Kovats index not exceeding 1600 (which may be called category B') are monofunctional compounds with molecular weights in the range 160 to 230.

A sub-set of particularly preferred fragrance materials within category B' is those with a Kovats parameter falling within the range 1350 up to 1600, and possessing a molecular structure containing a ring, such as phenyl or cycloalkyl.

A number of fragrance materials which fulfil the above criteria for category B' are listed in the table below. Materials which are in the particularly preferred sub-set are marked with an asterisk.

Examples of fragrance materials in category B'	
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	1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carbaldehyde*
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	1-(5',5'-dimethylcyclohexenyl)-pent-en-1-one*
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25	2-heptyl cyclopentanone*
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	2-methyl-3-(4'-tert-butylphenyl)propanal	
	2-methylundecanal	
	2-undecenal	
	2,2-dimethyl-3-(4'-ethylphenyl)-propanal	
5	3-(4'-isopropylphenyl)-2-methylpropanal	
	4-methyl-4-phenylpent-2-yl acetate*	
	allyl cyclohexyl propionate*	
	allyl cyclohexyloxyacetate*	
	amyl benzoate*	
10	methyl ethyl ketone trimers	(Azarbre, TM)
	benzophenone*	
	3-(4'-tert-butylphenyl)-propanal	(Bourgeonal, TM)
	caryophyllene*	
	cis-jasmone*	
15	citral diethyl acetal	
	citronellal diethyl acetal	
	citronellyl acetate	
	phenylethyl butyl ether	(Cressanther, TM)
	damascone, alpha-*	
20	damascone, beta-*	
	damascone, delta-*	
	decalactone, gamma-*	
	dihydro isojasmonate*	
	dihydrojasmone*	
25	dihydroterpinyl acetate	
	dimethyl anthranilate*	
	diphenyl oxide*	
	diphenylmethane*	
	dodecanal	
30	dodecen-2-al	
	dodecane nitrile	

	nerolin
	nonalactone gamma
	nopyl acetate*
	para tert-butyl cyclohexyl acetate
5	4-isopropyl-1-methyl-2-[1'-propenyl]-benzene* (Pelargene, TM)
	phenoxyethyl isobutyrate*
	phenylethyl isoamyl ether*
	phenylethyl isobutyrate*
10	tricyclodecenyl pivalate* (Pivacyclene, TM)
	phenylethyl pivalate* (Pivarose, TM)
	phenylacetaldehyde hexylene glycol acetal*
	2,4-dimethyl-4-phenyltetrahydrofuran (Rhubafuran, TM)
	rose acetone*
15	terpinyl acetate
	4-isopropyl-1-methyl-2-[1'-propenyl]-benzene (Verdoracine, TM)
	yara*
	(4-isopropylcyclohexadienyl)ethyl formate

20 Examples of fragrance materials which lie within category B, but have Kovats index above 1600 and so are outside category B' are listed in the following table:

	Within category B but outside category B'
25	amyl cinnamate
	amyl cinnamic aldehyde
	amyl cinnamic aldehyde dimethyl acetal
	cinnamyl cinnamate

contact with the axillae (armpits) of a panel of human subjects, and held there for a standard period of time. From subsequent olfactory evaluation by trained assessors, a Malodour Reduction Value can be
5 calculated so giving a measure of the effectiveness as a deodorant of the perfume under test.

Stage 1 is preparation of the perfume treated fabric. A test fabric is subjected to a textile finishing which applies perfume to the fabric
10 at a predetermined percentage of perfume composition, by weight of the cloth. A control fabric is given similar treatment, with or without perfume, depending on the purpose of the test. Depending on the purpose of the test, the fabrics may subsequently be washed
15 and dried.

The test and control fabrics are cut into 20cm x 20cm squares for testing.

Stage 2 is the carrying out of the test. A team of three Caucasian female assessors of minimum
20 age 20 years is selected to carry out olfactory evaluation on the basis that each is able to rank correctly the odour levels of the series of standard aqueous solutions of isovaleric acid listed below, and each is able to assign a numerical score,
25 corresponding to the odour intensity of one of these solutions, to the body malodour of a shirt insert

after has been worn in the axillary region by a male subject for a standard period of time.

A panel of 40 human subjects for use in the test is assembled from Caucasian male subjects of age within the range of from 20 to 55 years. By screening, subjects are chosen who develop axillary body malodour that is not unusually strong and who do not develop a stronger body malodour in one axilla compared with the other. Subjects who develop unusually strong body malodour, for example due to a diet including curry or garlic, are not selected for the panel.

For two weeks before the start of the test, the panel subjects are assigned an unperfumed, non-deodorant soap bar for exclusive use when washing and are denied the use of any other type of deodorant or antiperspirant. At the end of this period, the 40 subjects are randomly divided into two groups of 20.

The "test" and "control" fabric pieces are then tacked into 40 clean cotton or polyester cotton shirts in the underarm region in such a manner that in 20 shirts, the control fabric pieces are attached inside the left underarm region, and the test fabric pieces are attached in the right underarm region. For the remaining 20 shirts, the placing of control and test pieces of fabric is reversed.

The shirts carrying the tacked-in fabric

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inserts are then worn by the 40 panel members for a period of 5 hours, during which time each panellist performs his normal work function without unnecessary exercise.

5 After this five hour period, the shirts are removed and the inserts detached and placed in polyethylene pouches prior to assessment by the trained panel of assessors.

10 The malodour intensity of each fabric insert is evaluated by all three assessors who, operating without knowledge of which inserts are "test" and which are "control" and, without knowing the scores assigned by their fellow assessors, sniff each fabric piece and assign to it a score corresponding to the
15 strength of the odour on a scale from 0 to 5, with 0 representing no odour and 5 representing very strong odour.

20 Standard aqueous solutions of isovaleric acid which correspond to each of the scores 1, 2, 3, 4 and 5 are provided for reference to assist the assessors in the malodour evaluation. These are shown below:

SCORE	ODOUR LEVEL	CONCENTRATION OF AQUEOUS ISOVALERIC ACID (ML/L)
0	NO ODOUR	0

1	SLIGHT	0.013
2	DEFINITE	0.053
3	MODERATE	0.22
4	STRONG	0.87
5	VERY STRONG	3.57

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5 Further systems of selection are given in US-A-5482635
and US-A-5554588 also mentioned above.

10 US-A-5501805 describes perfume compositions made from a combination of fragrance materials, where the composition is a deodorant perfume yet has a relatively low odour. Such "low-odour" deodorant perfumes may be used in the present invention.

The test fabric is subjected to treatment with a fabric finishing liquor, containing perfume, so as to apply 0.5% of the perfume, by weight of the fabric. The control fabric is treated similarly, but

However, this test procedure can be operated
5 in other ways. To demonstrate the higher deposition of
perfume on spandex fibres, the control and test
fabrics are both treated with the same fabric
finishing liquor containing perfume. To isolate the
deodorant effect of the perfume, the test and control
10 fabrics can be the same, but no perfume is present in
the liquor used to treat the control fabric.

This model experiment demonstrates perfume deposition on spandex fibres. A mixture of perfume ingredients was prepared and added to an unperfumed, but otherwise conventional, laundry detergent powder, to provide a perfume concentration of 0.5% by weight.

The perfume was extracted from the dry cloths with organic solvent, and the content of the perfume ingredients in the solvent extracts was determined by gas chromatography. If the concentration

of an ingredient extracted from the spandex-containing cloth was greater than from the all-cotton cloth by a factor of 5 to 20, the result was coded as a medium enhancement (M). If the concentration was greater by 20 or more, it was coded high (H) and if less than 5 or not measurable, it was coded (L). The results obtained were as follows:

	Ingredient	K*	logP* *	Enhancement	Category
10	Boisambrene Forte	1714	5.5	M	B
	benzyl acetone	1206	2.0	M	-
	citronellol	1209	3.6	H	A'
	2,6-dimethyl-heptan-2-ol	975	2.9	L	-
15	jasmacyclene	1394	2.9	H	B'
	methyl salicylate	1167	2.3	L	-
	2-phenylethanol	1087	1.4	L	-
	terpinyl acetate	1331	4.0	H	B'
20	tetrahydrogeraniol	1180	3.6	H	A'
	tetrahydrolinalol	1083	3.5	H	A'
	Tonalid	1840	6.4	M	B
	yara	1416	3.2	H	B'

* Measured on OV-1 polydimethylsiloxane (Ohio Valley)
as stationary phase using capillary gc

** Measured or estimated using 'logP' software from ACD

25 Inc.

Kovats index of 1300 to 1600, so as to fall within category B'.

The cloths were then washed repeatedly, using a commercial detergent powder which included a different perfume. The washes were carried out using a Miele washing machine on its "Quickwash" programme at 40°C. 110gm of detergent powder was used for each wash. The fabric was rinsed three times after each wash and tumble dried.

The dried cloths were examined by a panel of expert assessors of perfume intensity. This was to determine the intensity of perfume on the fabric, but not its deodorant property. The results obtained were as follows:

	Odour Evaluation Scores					
	100% cotton			90% cotton and 10% spandex		
Washes:	1	3	5	1	3	5
Perfume U						
0%	2.0	2.4	2.8	4.0	4.4	4.6
1.0%	6.4	3.6	<3	16.0	14.0	12.8
0.1%	3.6	<3	<3	10.4	9.7	9.0
0.01%	3.2	<3	<3	8.8	8.0	7.2

It can be seen that the cloths which were not perfumed in the finishing treatment took up

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The cloths containing spandex fibres which were perfumed during the finishing treatment had a much higher level of perfume on them after one wash than the 100% cotton cloths. Even after five washes, the intensity of perfume on them exceeded the intensity of perfume on the 100% cotton cloths after one wash, and on the cloths which had not been perfumed prior to the first wash. Thus the spandex fibres were providing enhanced retention of perfume as well as enhanced deposition.

The 100% cotton cloths which had been perfumed during the finishing treatment were assessed again after 3 and 5 washes. The results showed that the level of intensity of the perfume was less than that observed after 1 wash but also showed that the olfactive differences between perfume U used in the finishing treatment and the perfume present in the washing powder was confusing the panellists.

Example 3

Two deodorant perfumes were used in treatment of cloths by a finishing process as in Example 2.

Category A: 30 wt% (all with Kovats index above 1600)

- 5 Category B: 68.5 wt% (13% with Kovats index 1300-
1600 and therefore within category B',
and 55.5 wt% with Kovats index above
1600).

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- Category A: 24.9 wt% (16.3 wt% with Kovats index 1050-1600 and therefore within category A', and 8.6 wt% with Kovats index above 1600)
- 15 Category B: 55.3 wt% (8.6 wt% with Kovats index 1300-1600 and therefore within category B', and 46.7 wt% with Kovats index above 1600).

The test cloths were: 100% cotton, 90% cotton with 10% spandex, 95% cotton with 5% spandex, 100% nylon and 82% nylon with 18% spandex. Perfume was used at a concentration of 0.5% based on the weight of the fabric. The treated cloths were tested for Malodour reduction in the test described earlier. The control cloths were 100% cotton, which had been subjected to the same finishing treatment, but without

perfume in that finishing treatment. The results are set out in the following tables, which show substantial enhancements of malodour inhibition when fabrics containing spandex fibres were used.

5 **Test 1:**

Fabric		perfume M (% by weight of fabric)	Malodour score	Malodour reduction	Malodour reduction as % of control
other fibre	spandex				
90% cotton	10%	0.5%	1.19	1.46	55%
100% cotton	0	0.5%	1.92	0.73	27.4%
82% nylon	18%	0.5%	1.00	1.65	62.1%
100% nylon	0	0.5%	1.97	0.68	25.5%
100% cotton (control)	0	0	2.65		

Notes: % malodour reduction calculated as 100%

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20      x(control score-sample score)/control score
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Statistical calculation showed that a difference in malodour reduction of 6.9% was significant at 95% level of confidence.

Test 2:

Fabric		perfume (% by weight of fabric)	Malodour score	Malodour reduction	Malodour reduction as % of control
other fibre	spandex				
95% cotton	5%	0.5% L	1.15	1.22	51.5%
95% cotton	5%	0.5% M	1.29	1.08	45.6%
100% cotton (control)	0	0	2.37		

Note: Statistical calculation showed that a difference in malodour reduction of 6.3% was significant at 95% level of confidence.

In test 1, malodour scores on 100% cotton fabric, with and without perfume, demonstrate a malodour reduction value of 0.73 attributable to the perfume. A similar malodour reduction value was observed when the test cloth was 100% nylon.

When spandex fibre was incorporated, the malodour reduction increased greatly, showing that increased deposition of perfume on spandex fibres compared with other fibres also provides an increased deodorant efficiency.

In test 2, similar high values of malodour reduction were obtained when either perfume L or

perfume M was used, in test fabrics with 5% by weight spandex fibres.

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